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## ***In Situ* X-Ray Absorption Study of Chromium Valency Changes in Passive Oxides on Sputtered AlCr Thin Films under Electrochemical Control**

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The valence state of chromium in passive films on metals is conventionally studied using surface analytical techniques such as AES and XPS. As these techniques involve electron detection, they can only be carried out *ex situ* in UHV after electrochemical treatment. X-ray absorption spectroscopy can be used to determine both valency and structural environment and, as only x-rays are involved, measurements can be carried out in air or *in situ* in an electrochemical cell. Recent *in situ* studies of passivity have used EXAFS (Extended X-ray Absorption Fine Structure) to determine passive film structure [1-4]. In this communication, we report on an *in situ* XANES (X-ray Absorption Near Edge Structure) study of reversible changes in the valence state of chromium in passive films,

A recent *ex situ* XANES experiment [5] showed that an oxide film containing Cr(VI) can be formed on AlCr alloys by polarization to high potentials in a borate buffer solution. This chromate was reduced to the +3 state at a low potential and then reoxidized to the +6 state by polarizing again to the high potential. In this communication we report similar results measured *in situ* which demonstrate the applicability of XANES to simultaneous valency and electrochemical measurements. As a single fixed specimen is used throughout the experiment, quantitative information on the dissolution of chromium is available.

## **EXPERIMENTAL**

Around the chromium K edge (~6keV), the absorption length of x-rays in water is of the order of 1mm which complicates cell design. The electrochemical cell is shown in Fig.1. It is based on that used by Kerkar *et al.* [1] which allows both electrochemical control and surface sensitivity. The electrode consists of a thin Mylar window (~6µm) on which has been sputtered ~100Å of Ta (in order to maintain electrical contact) and ~20Å of Al-12%Cr. The thin alloy deposit is used so that most of it is oxidized when the

passive layer is formed in order to minimize the signal from metallic chromium in the alloy. The electrode is in contact with bulk solution giving good electrochemical control.

A mercurous sulfate reference electrode was used (MSE, 656mV vs. SHE) and the solution was 0.5M  $\text{H}_3\text{BO}_3$  + 0.05M  $\text{Na}_2\text{B}_4\text{O}_7$ . Monochromatic x-rays were incident at  $\sim 45^\circ$  to the electrode surface and Cr  $\text{K}\alpha$  radiation was detected with a 13 element solid state detector (Canberra [6]) placed at  $90^\circ$  to the incident x-rays. Such an energy-discriminating detector is required in order to detect the small chromium fluorescence signal against the high background of incident radiation scattered by the cell, especially by the solution.

X-ray absorption edges of standard compounds, fine powders of  $\text{K}_2\text{CrO}_4$ , (Cr(VI)) and  $\text{Cr}_2\text{O}_3$  (Cr(III)), and chromium metal foil were measured in conventional transmission geometry using an ionization chamber detector.

## RESULTS AND DISCUSSION

The solid lines in Fig.2 show a series of absorption spectra measured *in situ* for chromium in the passive film on the sputtered Al-12Cr alloy. A linear background extrapolated from the pre-edge section has been subtracted. The spectra are shown on the same scale but have been displaced vertically for ease of viewing. The broken lines show the three standard compounds for comparison. These have been normalized to give the same edge height as the experimental data. These curves show that the position of the absorption edge moves to higher energies as the valence state of chromium increases. Curve (b) ( $\text{K}_2\text{CrO}_4$ ) shows the distinctive sharp peak below the edge which is characteristic of tetrahedrally coordinated Cr(VI) compounds. For a pure 6-valent compound, the height of the pre-edge peak is approximately the same as the height of the edge.

Curve (a) (solid line) shows the spectrum measured after the sample was immersed at open circuit for 12 minutes. The position of the edge coincides with that of chromium metal (broken line). Curve (b) shows the spectrum measured 7 minutes after the potential was stepped to 2V(MSE). From the height of the pre-edge peak and the position of the edge, it can be seen that about half the chromium is in the +6 valence state. Comparison of the edge heights of (a) and (b) show that there is little loss of chromium when it is oxidized in the film to the +6 valence state despite the solubility of chromate ions.

Curve (c) shows the spectrum measured after the specimen is then reduced at -1.5V(MSE) for 6 minutes. Comparison with the  $\text{Cr}_2\text{O}_3$  standard (broken line) indicates that the chromium is in the +3 valent state with no +6 present. The height of the edge is similar for curves (a), (b), and (c) indicating that the oxidation-reduction cycle has resulted in insignificant dissolution of chromium.

## CONCLUSION

X-ray absorption can be used to make *in situ* valence measurements of species in passive films under electrochemical control. This technique has been used to show that the valence state of chromium in passive films on a sputtered AlCr alloy can be changed reversibly without dissolution of 6-valent chromium.

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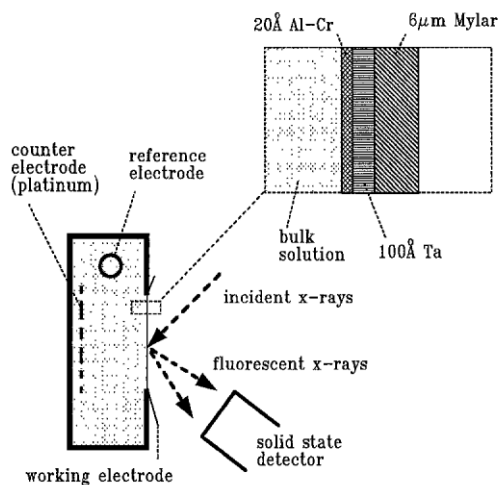


Fig.1 Schematic plan of experimental apparatus.

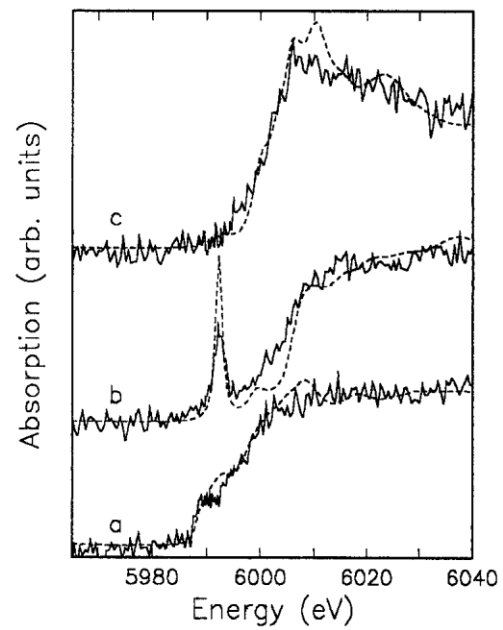


Fig.2 X-ray absorption spectra measured *in situ* for a Al-12Cr alloy (a) at open circuit, (b) after 7 minutes at 2V(MSE), (c) after 6 minutes at -1.5V(MSE) (solid lines). The broken lines show standard compounds measured in transmission: (a) Cr metal, (b) K<sub>2</sub>CrO<sub>4</sub> powder and (c) Cr<sub>2</sub>O<sub>3</sub> powder.